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BULLETIN NO. 79

Experiments on the Cause and Avoidance of Injury to Foliage in the Hydrocyanic Gas Treatment of Trees.

In University Experiment Station Bulletin No. 71, it was shown that hydrocyanic acid gas could be used effectively against scale insects; but that the tree suffered by the treatment. In a subsequent bulletin (No. 73), it was shown that the injury to the foliage of citrus trees could be prevented by the use of carbonic acid gas, injected at the same time with the hydrocyanic. The cause of this preventive action was not readily explained and its failure to protect on very hot days, showed that something remained to be done in perfecting the treatment; furthermore, the additional trouble and expense of this improved treatment made it highly desirable to seek for some easier means of saving the foliage.

The investigations here recorded were made from time to time during November, December and January of 1887-8, in order to find out what caused the injury, and likewise to explain the protective action of the carbonic acid used in the later experiments. The general manner of treatment as applied on a large scale, was followed in each operation;* and suitable apparatus was devised for carrying out the details. A barrel of about five cubic feet capacity was used as a chamber to replace the tent. A small bellows was used to produce the necessary circulation, and a glass bottle, into which was inserted a closed funnel holding the proper doses, served as a generator. A small Woulffs (three-necked) bottle served the purpose of a "relay," where the gases could be mixed, or material for drying them inserted. The temperature was indicated by thermometers placed in the top of the chamber.

A half-dozen orange branches set in pots, and a dozen well-potted orange seedlings, were used to experiment upon. The former were used to obtain some preliminary measure of the quantity of materials to be employed in the later treatments.

THE FOLLOWING TABLE SHOWS THE ARRANGEMENT OF THE SEVERAL EXPERIMENTS; NUMBERED FOR REFEREECE.

No. of Exp't.	Materials Used.	Method of Treatment.	Temp. Deg. Fahr.	Remarks.
1	Not treated	.....	....	
2	Cyanide	Wet	60	
3	Cyanide + Carbonate	Wet	59	
4	Cyanide	Dry	58	
5	Cyanide + Carbonate	Dry	59	
6	Cyanide	Wet	58	
7	Cyanide	Wet	59	
8	Cyanide + Carbonate	Wet	59	
9	Cyanide	Dry	66	
10	Cyanide + Carbonate	Dry	67	
11	Cyanide	Wet	64	Sprayed.
12	Cyanide + Carbonate	Wet	63	Sprayed.
13	Cyanide	Wet	100	
14	Cyanide + Carbonate	Wet	103	
15	Cyanide	Dry	109	
16	Cyanide + Carbonate	Dry	106	
17	Cyanide	Wet	102	Sprayed.
18	Cyanide + Carbonate	Wet	97	Sprayed.
19	Ammonia determination	.....	....	
20	Cyanide	Dry	59	
21	Cyanide	Dry	55	
22	Cyanide	Wet	54	
23	Cyanide	Wet	56	
24	Cyanide	Wet	56	
25	Cyanide	Wet	56	Gas dried.
26	Cyanide	Wet	63	
27	Cyanide + Ammonia	Wet	55	
28	Cyanide + Ammonia	Wet	67	
29	Cyanide + Ammonia	Wet	62	Mixed in chamber.
30	Formic Acid + Ammonia		50	
31	Formic Acid		53	

The second column shows the material em-

*It should be noted that an essential point in the mode of operating, first practiced by me at San Gabriel in the spring and summer of 1887, was the use, at the suggestion of Prof. Hilgard, of a pump or blower for the purpose of mixing the gases generated, with the air in the tent, by continuous circulation; thus avoiding injury from the effects of overdoses at some points while leaving others without adequate treatment, as must inevitably happen where no such equalizing appliance is used. It was doubtless from this cause that experiments previously made by others (understood to have employed hydrocyanic gas) were not satisfactory.

ployed; the third indicates whether they were used in the solid condition (dry), or in solution (wet).

When operating in the "dry" way the salts were used in the solid form, and usually the gas was further dried and freed from ammonia by passing it through strong sulphuric acid. In operating in the "wet" way, *solutions* of the salts were used and the gas was passed directly into the chamber, except in one or two cases where the gas was subsequently dried. The fourth column indicates the temperature at which the air in the chamber was kept.

In No. 1 an orange limb was used, potted like the others and left untreated to serve as a check. It remained in good condition throughout the time of experimenting.

In the numbers following, the conditions were varied both by changing the manner of treatment and materials used. The doses used were larger in proportion than those used in field-work, in which it was shown that small trees required proportionately larger doses than large ones.

In several cases the trees and the inside of the chamber were sprayed with water, to note the effect of the gas upon wet trees, and also to note that of the water upon the gases themselves.

Production and Effects of Ammonia.

It is known that when cyan*ates* are present in generating hydrocyanic gas, more or less *ammonia* is produced. In the materials used for these experiments, this may have been the case. Furthermore, under certain conditions, ammonia may be produced in the treatment of simple cyanide with acid. Preliminary tests were made to demonstrate these facts, and to study the reactions when applied in various ways, as well as to determine the best mode of using the materials. For the intense scalding effects of ammonia upon the foliage had been noted in my former experiments (see Bulletin No. 71), and it was conjectured that this gas, unintentionally produced, might be concerned in causing injury in cases not otherwise easily explained.

As previously reported, it was found impracticable to use the cyanide of potassium without first dissolving it, and that it was necessary to keep the carbonate of soda well mixed with the cyanide, so that the reaction upon both would occur at the same time. But it was further shown that the alkaline reaction of the gas, due to ammonia, is produced only when the solution, instead of the solid cyanide, is used; *rapid* addition of the acid to the dry salt, or *vice versa*, invariably produced an *acid* gas, while the *slow* mixing of the two materials in solution invariably produced decided *alkalinity*, often to a very harmful degree. The amount of ammonia was found to be variable, perhaps largely because a part was masked by the hydrocyanic acid produced during the violent action that takes place when the acid is added rapidly to the solution.

All the experiments with the dry cyanide alone showed but slight injury to the foliage, and a slightly increased injury was noted on the plants treated with the cyanide *solution* alone. When the carbonate of soda was used with the cyanide in the solid form or in solution, the injury to foliage was in either case very materially lessened. Passing the gas through sulphuric acid produced results similar to those of the carbonate treatment, viz.: immunity to the foliage.

Indications having thus pointed toward ammonia as the cause of the injury, some direct experiments were made with this gas. In the first ammonia-treatment the gas was separately generated and mixed with the hydrocyanic gas from an ordinary treatment, the mixed gases being conducted into the chamber.

The intensely acid action of the gas leaving the hydrocyanic generator at once turned to the alkaline, and so continued in the chamber, thus showing that a certain moderate excess of ammonia was present. Decidedly injurious effects upon the foliage were quickly noted.

In this experiment the ammonia and cyanide gases were mixed in the "relay." In order to leave more of the ammonia free to act upon the foliage, it was injected directly into the chamber, where the two gases were less intimately mixed. Upon circulating the gas, strong alkalinity prevailed in all parts of the apparatus and the atmosphere about the tree was decidedly charged with ammonia. The results were very marked. In a short time the trees wilted; in 10 days all the foliage was crimped up and later all fell off. Even the wood of the more tender branches was noticeably affected.

As *formic acid* is often produced during the decomposition of a cyanide, an experiment was made to determine its effect upon foliage. A solution of the acid was boiled and the vapor was conducted into the chamber until a quite decided acid reaction was shown by the test papers. No harmful effect was noticeable. Formic acid and ammonia were next separately introduced, the ammonia being in very slight excess. In this case also no noticeable harm was done.

Influence of Temperature.

It is to be regretted that the normal temperature (50° to 65° F.) during the experiments was much lower than that which would be met with in actual field-work; and therefore the injury done to the seedlings would not be so marked as in the latter case.

An attempt was made to raise the temperature within the chamber up to that of a warm summer's day in the orange districts. The range of temperatures used was 95° to 105° F., but the outside temperature being low, as soon as circulation began, the moisture from the interior of the chamber, given off during the rise in temperature, was partially drawn in and condensed in the tubes during the circulation, and thus absorbed the ammonia as well as part of the hydrocyanic gas.

Notwithstanding this partial removal of ammonia by absorption, the results showed that these high-temperature treatments produced more injurious effects than similar treatments at lower temperatures.

Conclusions.

From the foregoing experiments we are led to believe that *ammonia* has been the fruitful cause of the injury to the trees subjected to the treatment under discussion. Under this view of the case, the beneficial effects of the use of carbonic acid gas would seem to be due to its power of neutralizing the ammonia, with the formation of carbonate of ammonium, when the

two gases come together. And, furthermore, the failure of the carbonic acid to *completely* preserve the tree during the hot part of the day follows from the easy decomposition, by heat, of the carbonate of ammonium, which does not occur during treatments at lower temperatures. Even the formate of ammonium, produced in a preceding experiment, would be decomposed in a like manner and some ammonia set free to act upon the foliage.

Modes of Preventing Injury.

There are, then, two means of averting the injury to the foliage: *First*, by the use of the dry salt; *second*, by the use of proper appliances to absorb the ammonia as it leaves the generator.

In the first case, viz.: Using the dry salt, only a minimum amount of ammonia is produced during a strong reaction. But it was shown that it is quite impossible to handle the dry salt so as to insure complete action of the whole dose; and furthermore, the slowness of the action prevents the rapid injection of the gas into the tent. It should be injected rapidly so that complete circulation of the gas about the tree may be established and the maximum effect produced at once, so as not make it necessary to increase the time of exposure.

In the second case, viz.: the use of the solution, the action is rapid and the injection can take place immediately. But with the use of solution, the trouble from formation of ammonia comes in. This can be obviated by the use of the proper apparatus to absorb the ammonia as it leaves the generator.

The apparatus used in field-work can be so modified that an absorbent of the ammonia may be inserted at the exit of the generator and connected with the general circulation. Such an apparatus can be made of a cylinder filled with loose pumice-stone over which sulphuric acid is poured from time to time. By this means a large surface is exposed for the absorption, and it can be readily so arranged that with slight trouble the surface of the pumice-stone can be re-saturated with sulphuric acid.

This apparatus, if interposed in the tubes through which the general circulation takes place, would interfere with the rapid passing of the volume of air which is to accomplish the agitation within the tent. In order to avoid this obstruction, a secondary circuit may be connected with the general circulation, to be used only when the generator is to be cleared of the last portion of the hydrocyanic gas. The pressure of the gas alone during its evolution is sufficient to force its way slowly into the general circulation. Thus the general circulation and agitation remain independent of both generator and drying-chamber. The secondary circuit carries a volume of air from the blower through the generator and through the drying-vessel and thence discharges into the general circulating pipe. This is accomplished by placing a hinged valve at the exit opening of the blower into the circulating tube in such a manner that the current of air may be passed either forward or backward by reversing the motion of the blower. The air may be forced by the backward movement through the secondary circuit.

By the application of either of the above methods the use of carbonate of soda can be avoided, and the work somewhat simplified. There will be far less residue in the generator, so that several treatments may be made without emptying the latter. Beside this there will be a decrease in the expense through the omission of the carbonate and the correspondingly less amount of sulphuric acid required.

It will be necessary to demonstrate by further experiments whether the use of the cyanide alone will be so effective against the scale as when combined with carbonic acid. The best results of field experiments have accompanied the joint use of carbonate and cyanide, although it is maintained that the cyanide alone will produce as fatal effects upon the insect.

Some tests were incidentally made to note the effect of the gas upon the scale insects *Aspidiotus* and *Lecanium*. Branches of laurel and acacia infested with these scales were placed in the chamber during the treatment of trees at higher temperatures. The effect in some instances was complete, while in others 90 per cent of the insects were killed and the remaining 10 per cent still showed faint signs of life and may have survived the treatment. Under the proper treatment this gas remedy will undoubtedly prove as effective on these scales as upon the white scale, against which the remedy was originally intended to be applied.

Berkeley, May 5, 1888. F. W. MORSE,